DETECTION OF ORGANIC CONSTITUENTS INCLUDING CHLOROMETHYLPROPENE IN THE ANALYSES OF THE ROCKNEST DRIFT BY SAMPLE ANALYSIS AT MARS (SAM). J. L. Eigenbrode[1], D. Glavin[1], P. Coll[2], R. E. Summons[3], P. Mahaffy[1], D. Archer[4], A. Brunner[1], A. Buch[5], M. Cabane[6], P. Conrad[1], C. Freissinet[1], M. Martin[1], C. McKay[7], K. Miller[3], R. Navarro-González[8], A. Steele[9], C. Szopa[6], S. Teinturier[6], J. Hurowitz[10], J. Evans[10], M. Anderson[10], L. Jandura[10], K. Brown[10], C. Logan[10], S. Kuhn[10], R. Anderson[10], L. Beegle[10], B. Blakkolb[10], I. Katz[10], D. Limonadi[10], R. Rainen[10], J. Umland[10], the SAM team, and the MSL Science Team, [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, jennifer.l.eigenbrode@nasa.gov, [2]LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France, [3]Massachusetts Institute of Technology, Cambridge, MA 02139, [4]NASA Johnson Space Center, Houston TX 77058, [5]Ecole Centrale Paris, 92295 Chatenay-Malabry, France, [6]LATMOS, Univ. Pierre et Marie Curie, Univ. Versailles Saint-Quentin & CNRS, 75005 Paris, France, [7]NASA Ames Research Center, Moffett Field, CA 94035, [8]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, [9]Carnegie Institution of Washington, Washington, DC 20015. [10]Jet Propulsion Laboratory, Pasadena, CA 91011.

Introduction: A key challenge in assessing the habitability of martian environments is the detection of organic matter—a requirement of all life as we know it. The Curiosity rover, which landed on August 6, 2012 in Gale Crater of Mars, includes the Sample Analysis at Mars (SAM) instrument suite capable of *in situ* analysis of gaseous organic components thermally evolved from sediment samples collected, sieved, and delivered by the MSL rover. On Sol 94, SAM received its first solid sample: scooped sediment from Rocknest that was sieved to <150 µm particle size. Multiple 10-40 mg portions of the scoop #5 sample were delivered to SAM for analyses. Prior to their introduction, a blank (empty cup) analysis was performed. This blank served 1) to clean the analytical instrument of SAM-internal materials that accumulated in the gas processing system since integration into the rover, and 2) to characterize the background signatures of SAM. Both the blank and the Rocknest samples showed the presence of hydrocarbon components.

The Rocknest aeolian drift: Rocknest, located in Gale Crater, consists of an inactive, sandy wind drift mantled with dust [1]. Rocknest was chosen as the first solid sample site because it was believed to be broadly similar to aeolian sand/dust deposits studied by MER, and because this material was ideal for decontamination of the Sample Acquisition/Sample Processing and Handling (SA/SPaH) hardware [2]. Although wind-transported surface sediments provide poor conditions for organic matter preservation, they do not preclude the presence of recent meteoritic organic material.

SAM measurements: SAM heated samples up to ~840° C under helium. The evolved gases were sniffed directly by the quadrupole mass spectrometer (QMS; experiment called evolved gas analysis, EGA) then adsorbed in a trap where they were later released by flash heating to the gas chromatograph (GC) for molecular separation, followed MS detection.

Hydrocarbons detected via EGA. Masses diagnostic of inorganic and organic gases were detected via EGA. In particular, O_2, likely released from the thermal breakdown of a (per-)chlorate mineral [3], and reaction products of N-methyl-N-t-butyldimethylsilyl-trifluoroacetamide (MTBSTFA) and dimethylformamide (DMF) reagents in SAM wet chemistry cups were detected [4]. Notably, a variety of other masses (Fig. 1) from organic molecules were detected in the Rocknest samples, but were largely near or below detection limits and showed a different thermal profile in the blank. The blank data cannot account for all of the organic signatures observed in the Rocknest sample. However, a similar set of masses with the same evolution character as the Rocknest sample were detected in lab EGA experiments analyzing fused silica with 1 wt% $MgCl_2O_8$ and MTBSTFA (not shown).

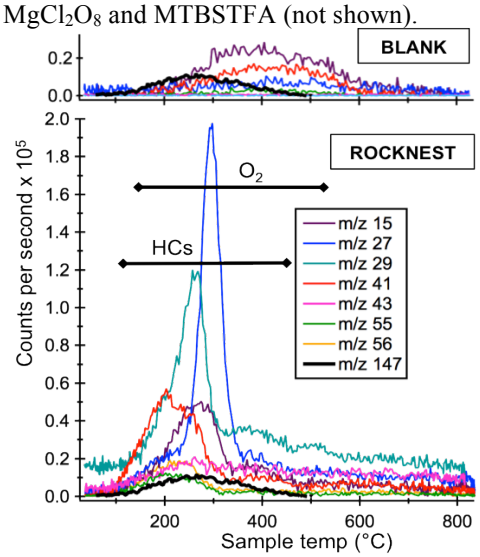

Figure 1. SAM EGA pyrograms of the blank and the first Rocknest sample showing a representative set of ions common of organic molecules. Rocknest organic signatures can not be explained by the blank alone. In the Rocknest data, most organic components evolve below 500° C overlapping with O_2 evolved from chlorate minerals and MTBSTFA reaction products (represented by m/z 147).

Chloromethylpropene detected via GCMS. A vast majority of the GCMS signature for Rocknest matches the blank, but is inconsistent with EGA results indicating a variety of organic fragments that are not present in the blank. Four compounds were identified in the Rocknest GCMS data that are not in the blank: mono-, di-, and tri-chloromethanes [5] and chloromethylpropene (a C4 chlorinated hydrocarbon). Chlorinated C2, C3, and C5 hydrocarbons were not detected. Chloromethylpropene was identified by mass spectra comparison of processed data [6] and the NIST library (Fig. 3).

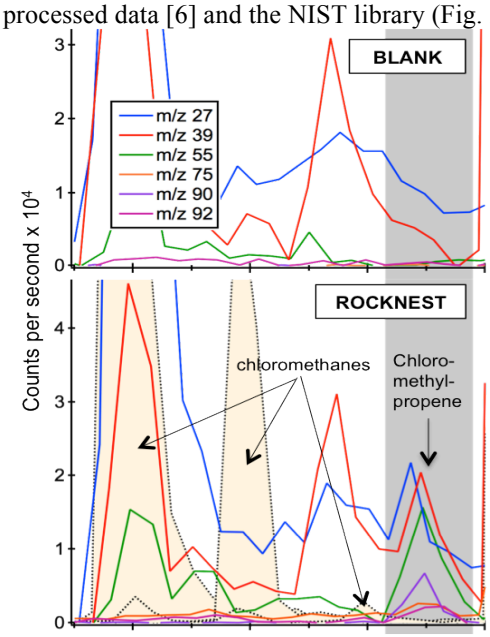

Figure 2. SAM GCMS ion chromatograms of the blank compared to the Rocknest sample showing a peak in Rocknest that is absent in the Blank (grey shaded region). Chloromethanes (m/z = 50, 84, and 83 respectively) are shown for reference (yellow shaded peaks).

Discussion: The disparity in the EGA and GCMS observations for organics detected in Rocknest data that are not explained by the blank may be indicating that gases are condensing, ineffectively trapping, unstable, or are simply not amenable to passage through the GC. Lab analyses suggest that most of the organic signature in the EGA data may be attributed to MTBSTFA reacting with oxychloride compounds (e.g. perchlorates) or associated thermal breakdown products (Cl_2, HCl, and O_2). Although the chloromethanes source is still under investigation [5], chloromethylpropene most likely a reaction product of the tert-butyl group in MTBSTFA and chlorine. Rearrangement and H-elimination reactions produce chloromethylpropene during thermolysis or upon ionization in the QMS. This process excludes the formation of C2 and C3 chlorohydrocarbons. Formation of >C5 chlorohydrocarbons from MTBSTFA is highly unlikely.

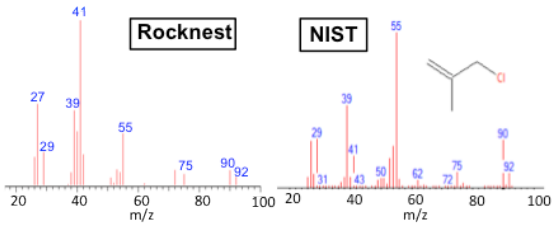

Figure 3. Chloromethylpropene mass spectra: Rocknest vs. NIST.

Another possible organic source considered was the MSL sampling chain (SA/SPaH). Rigorous cleaning and monitoring of SA/SPaH from scoop (the drill was not used at Rocknest) to the sample portioner suggest this source is unlikely. Estimates for sample-chain derived contamination in the Rocknest scooped sample are 8-13 ng/g, based on Fourier transform infrared spectroscopy analyses of swabs wiped across contact surfaces [2]. A similar swab extract was analysed by pyrolysis-GCMS and yielded no detectable organic components. Thus, there are no data to support the MSL sampling chain being a significant source of organics that might account for the Rocknest EGA observations and nanomole levels of chlorohydrocarbons detected by GCMS [5].

It is possible that a portion of the organic signatures observed in the Rocknest data are from indigenous martian organic matter. However, if it is present, it is in concentrations lower than the current SAM background and will be difficult to confirm.

Conclusions: The SAM EGA and GCMS experiments at Rocknest were repeatedly successful. The organic components detected in Rocknest data have carbon structures (chloromethanes and chloromethylpropene) that may have originated from the SAM instrument and subsequently reacted with a oxychloride compounds in the Rocknest sample. It is possible that the presence of SAM background components and reaction products could be obscuring detection of ppb levels of martian organic constituents, if they are present. SAM has made no definitive detection of organic materials indigenous to the Rocknest sample. The SAM team is optimizing experiments to improve sensitivity to low levels of organics in future samples.

References: [1] Edgett, K.S. et al. (2013) *this meeting.* [2] Anderson, M. et al. (2012) *Rev. Sci. Instrum. 83*, 105109. [3] Sutter, B. (2013) *this meeting.* [4] Freissinet, C. et al. (2013) *this meeting.* [5] Glavin, D. P. et al. (2013) *this meeting.*[6] Brunner, A. et al. (2013) *this meeting.*

Acknowledgements: J.E., D.G., R.S. and K.M. are funded by the NASA ROSES Mars Science Laboratory Participating Scientist Program.